CALCULATION OF *f*-VALUES OF POTASSIUM ATOM

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ABSTRACT. Employing the empirical and the Hartree fields, the *f*-values of potassium atom have been determined. The Schroedinger equation was integrated by Stoermer's numerical method using close-type formula given by Milne. (A simple interpolation formula for altering the argument interval is also given.) A striking feature of the calculation is that the *f*-value of the first line is greater than unity.

Demands of the sum rule suggest that contribution towards *f*-value by the continuous absorption at the head of the series limit must be .05, *i.e.*, much larger than the expected value of .0002 from the monotonic curve obtained theoretically by Miss Phillips (1932). It appears, therefore, that the extrapolation of this curve is not warranted. Ditchburn's recent experiments showing marked increase in atomic absorption on high frequencies seem to support this view.

Hargreaves (1929) has shown that the oscillator strengths of any absorption line due to a transition from the level s to the excited level r, is given by

$$f_{r\,s} = \tfrac{1}{3}(\nu_{r\,s}/\mathrm{R}ca^2)\,\frac{1}{g_s}\,\Sigma|\mathrm{I}_{r\,s}|^2 \qquad \ldots \quad (1)$$

where $\nu_{r\,s}$ is the frequency of the radiation, R the Rydberg constant and a the Bohr radius of one quantum orbit of Hydrogen, $\mathrm{I}_{r\,s}$ is the matrix amplitude of the transition s to r. Summation is for any degeneracy in the levels, which can be neglected here as the determination is to be for the doublets as a whole. Matrix amplitude is known from the eigen-functions of each level. The eigen-functions for potassium can be calculated following the work of Trumpy (1929) on lithium and of Prokofjew (1929) on sodium. The advantages and limitations of the method have been discussed by the latter. The method with some modifications is given below.

For the case of an atom with centrally symmetrical field, the eigen-functions (neglecting spin and relativity effects) are represented as

$$\psi_{n,l,m} = \mathrm{X}_{n,l}(r)\mathrm{Y}_{l,m}(\theta)e^{im\phi}$$

where $\mathrm{Y}_{l,m}(\theta)$ are the Legendre functions. The function $\mathrm{X}_{n,l}(r)$ satisfies the equation

$$\frac{d^2\mathrm{X}_{n,l}}{dr^2} + \frac{2}{r}\frac{d\mathrm{X}_{n,l}}{dr} + \frac{8\pi^2 m}{h^2}\left[\mathrm{E}_{n,l} - \mathrm{V} - \frac{l(l+1)}{r^2}\right]\mathrm{X}_{n,l} = 0 \qquad \ldots \quad (2)$$

where V is the potential energy in the central field and E is the eigen-value of the state in question. To solve this equation a knowledge of the eigen-values and potential functions is required for which the equations have continuous, finite and single-valued solutions. For the purposes of the present study it is important to use the observed, actual term values and make any required adjustments only in the theoretical field to be used, say Hartree field. But for the empirical field as given earlier by the author (Nanda, 1944) any special corrections are not needed. Thus, for $\mathrm{E}_{n,l}$ we may put $-\mathrm{W}_{n,l} = -hc\nu_{n,l}$ where $\nu_{n,l}$ is the

term-value for n_l in wave numbers. It is possible, then, by a numerical method to solve the equation for any term-value.

Due to the finite interval in numerical integration, and also due to any slight inaccuracy of the field, the eigen-functions may not exactly fulfil the boundary conditions, especially rX may not come out exactly zero at $r=0$. This can be achieved by very slight modification of the field, and in fact, the magnitude P at $r=0$ was never larger than 1% of the largest amplitude.

To solve the wave equation (2) substitute $r=a\rho$ and $P=\rho X_{n,l}$; ρ being r/a, and $V=\frac{Q}{\rho^2}$ where Q is the field function obtained elsewhere in the form $\alpha\rho^2+\beta\rho+\gamma$. The wave equation becomes

$$\frac{d^2P_{n,l}}{d\rho^2}+\left[2\alpha+\frac{\nu^2_{n,l}}{R}+\frac{2\beta}{\rho}+\frac{2\gamma-l(l+1)}{\rho^2}\right]P_{n,l}=0 \qquad \ldots (3)$$

R is the Rydberg constant. At large ρ where the wave function assumes an asymptotic form, we can write the solution as follows :

$$P_{n,l}=e^{-\frac{1}{2}\lambda\rho}\rho^{k}\left\{1+\frac{\mu^2-(l+\frac{1}{2})}{\lambda}+\frac{[\mu^2-(l+\frac{1}{2})^2][\mu^2-(l-\frac{1}{2})^2]}{1.2.\lambda^2}+\ldots\right\} \qquad \ldots (4)$$

where $\lambda=2\rho\sqrt{\frac{\nu_{n,l}}{R}-2\alpha}$; $k=\frac{\beta}{\sqrt{\frac{\nu_{n,l}}{R}-2\alpha}}$; $\mu^2=\frac{1}{4}-[2\gamma-l(l+1)]$

writing equation (3) in the form

$$\frac{d^2P_{n,l}}{d\rho^2}=f(P_{n,l},\rho) \qquad \ldots (5)$$

we can construct the table (I) for

$$P_{n,l} \text{ and } \xi_i=h^2f(P_{n,l},\rho_i) \qquad \ldots (6)$$

where $h=\rho_i-\rho_{i-1}$; and their backward differences, given by the relation $\Delta^r v_i=\Delta^{r-1}v_i-\Delta^{r-1}v_{i-1}$. The accuracy is not appreciably increased by extending the table beyond $\Delta^4\xi_i$.

TABLE I

ρ_i	$P_{n,l}$	ΔP_i	Δ^2P_i	ξ_i	$\Delta\xi_i$	$\Delta^2\xi_i$	$\Delta^3\xi_i$	$\Delta^4\xi_i$
ρ_1	P_1			ξ_1				
ρ_2	P_2	ΔP_2		ξ_2	$\Delta\xi_2$			
ρ_3	P_3	ΔP_3	Δ^2P_3	ξ_3	$\Delta\xi_3$	$\Delta\xi_3$		
ρ_4	P_4	ΔP_4	Δ^2P_4	ξ_4	$\Delta\xi_4$	$\Delta\xi_4$	$\Delta\xi_4$	
ρ_5	P_5	ΔP_5	Δ^2P_5	ξ_5	$\Delta\xi_5$	$\Delta\xi_5$	$\Delta\xi_5$	$\Delta\xi_5$
...	...	...	...	...	...	...	...	...
...	...	...	...	...	...	...	...	...
ρ_i	P_i	ΔP_i	Δ^2P_i	ξ_i	$\Delta\xi_i$	$\Delta^2\xi_i$	$\Delta^3\xi_i$	$\Delta^4\xi_i$

After putting down a few values from asymptotic expression at large distances, the integration ahead towards lesser distances is carried out in the following manner. Stoermer's formula gives a trial value of $\Delta^2 P_i$ by the relation

$$\Delta^2 P_i = \xi_{i-1} + \tfrac{1}{12}(\Delta^2 \xi_i + \Delta^3 \xi_i + \tfrac{19}{20}\Delta^4 \xi_i + \ldots) \qquad \ldots (7)$$

Simple addition or subtraction in the first two columns of the table yields a trial value of $P_{n,l}(\rho_i)$. Using this value of $P_{(i)}$ and the field Q we get ξ_i from equation (6) and right hand side of the table is completed as a trial value. Now a check is applied by the closed type formula (Milne, 1933) which requires

$$\Delta^2 P_i = \xi_{i-1} + \tfrac{1}{12}(\Delta^2 \xi_i - \tfrac{1}{20}\Delta^4 \xi_{i-1} + \ldots) \qquad \ldots (8)$$

Thus, the trial value is altered till the formula (8) is satisfied.

The starting point in this computation is so chosen that the value of P is very small, below significance so far as the main body of the P column is concerned. To save labour, the value of the interval for ρ may be as large as unity in the region $\rho > 2$, since the field function Q is same in the region greater than $\rho = 6.31$ and further, between $\rho = 1.90$ and $\rho = 6.31$ it is given by a single expression. It is only between $\rho = 0$ to $\rho = 1.9$ that there are five different expressions for Q, and so below $\rho = 1.9$ the interval should be small, say .1. To interpolate P between the interval ρ_i and ρ_{i-1} for a small fraction $x/h = p/10$ (let) above the ith point, the formula that can be best used is given below:

$$P_{i-p/10} = P_i - \left(p\frac{\Delta P_i}{10} + \frac{p(10-p)}{\lfloor 2} \frac{\Delta^2 P_i}{10^2} + \frac{p(10-p)(20-p)}{\lfloor 3} \frac{\Delta^3 P_i}{10^3} + \ldots \right). \qquad (9)$$

The values at $\rho = 2.4, 2.3, 2.2, 2.1$ are known and further integration can be

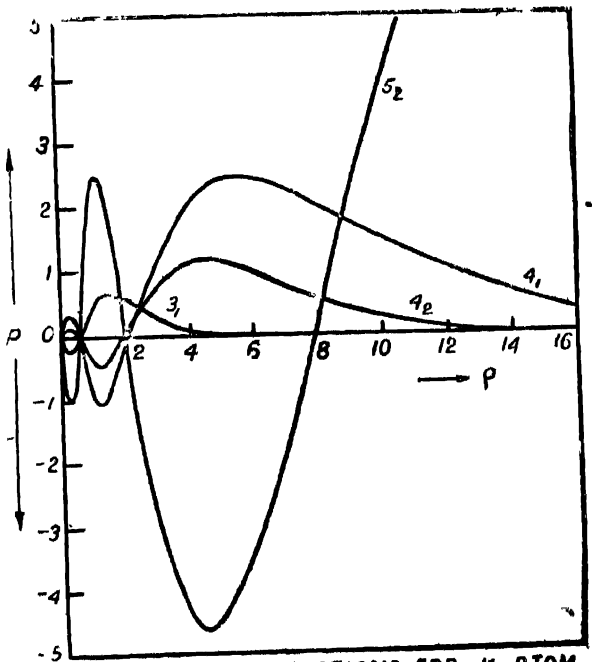

FIG 1(a) WAVE FUNCTIONS FOR K ATOM (UNNORMALISED)

carried out for $h'=.1$. In this manner, the eigen-functions $P(\rho_i)$ have been determined for the levels 4_0, n_1 (n from 2 to 8). See figure 1(a) and 1(b).

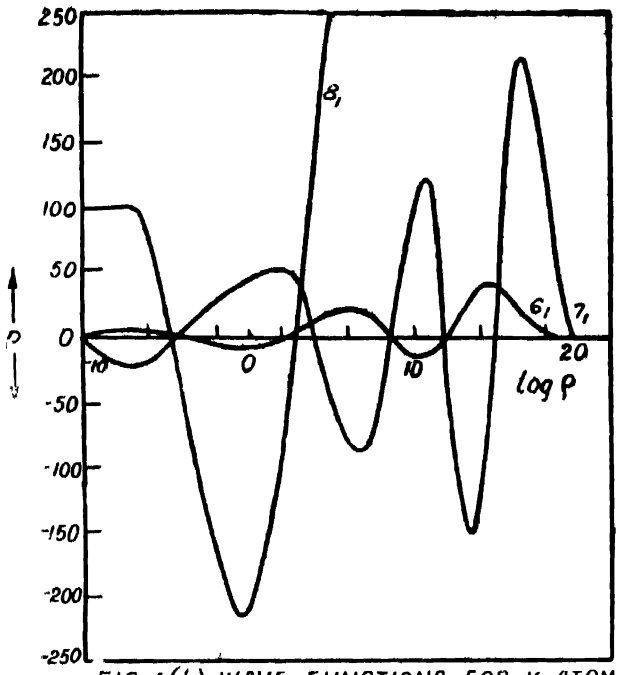

FIG. 1(b) WAVE FUNCTIONS FOR K ATOM (UNNORMALISED)

It can be shown that the square of the matrix amplitude $|I|^2$ for the transition 4, 0 to n, 1 is given by the relation

$$|I|^2=a^2\left\{\frac{(\int_0^\infty \rho P_{n,1}\, P_{4,0}\, d\rho)^2}{\int_0^\infty P_{n,1}^2\, d\rho \int_0^\infty P_{4,0}^2 d\rho}\right\}=a^2 S_{n,1;\,4,0} \qquad (10)$$

substituting the above in (1), we get

$$f(4,0 \rightarrow n,1)=\frac{1}{3}\,\frac{\nu_{n,1\rightarrow 4,0}}{R}\,S \qquad \ldots\ (11)$$

where ν is the absorbed frequency in wave numbers. The integrals for knowing S were found graphically. For higher levels, the integration may be done numerically by well-known Durand's rule or Simpson's rule.

The calculated f-values are given in Table II. In order to study the effect of any change in the field, the calculations were repeated with the Hartree field and the values with this field are given in column four of the table. However, since the boundary conditions for P at $\rho=0$ were much better observed by the use of the empirical field than with the uncorrected Hartree field (1934), the empirical field values should command greater reliance.

TABLE II

No.	Transition n,l to n,l	f-value empirical field	f-value Hartree field
1	4,0 to 4,1	1.08	1.02
2	4,0 to 5,1	1.18×10^{-2}	1.33×10^{-2}
3	4,0 to 6,1	2.5×10^{-3}	3.1×10^{-3}
4	4,0 to 7,1	3.1×10^{-3}	3.2×10^{-3}
5	4,0 to 8,1	6.6×10^{-6}	6.0×10^{-6}
6	4,0 to 2,1	-3.55×10^{-3}	-2.83×10^{-3}
7	4,0 to 3,1	-1.45×10^{-2}	-1.07×10^{-2}

The inverse transitions (6) and (7) are calculated on the assumption that the wave functions are separable.

DISCUSSION

1. A striking feature of the calculations is that the f-value of the first line is greater than unity. This is not against the sum rule of Thomas and Kuhn, since the inverse transition 4.0 to 3,1 is quite strong. It will be of interest to verify this point experimentally by a new determination of the absolute f-value of this line. The value observed by Weiler (*loc. cit.*) from observations on anomalous dispersion by Hook method is 1.00.

2. Ratio of f-values for the first two lines is 91·5 (empirical field) and 76.7 (Hartree field). The experimentally observed value from the Hook method is 111.5 (Prokofjew and Gamow (1927), and 98.5 Weiler (1929). Only the first two lines have been studied in this manner. There is no experimental data on observations in total absorption. Experiments, however, are in progress in this Laboratory to study the total absorption of these lines on infra red photographic plates.

3. Ratio of the third line to the fourth is slightly less than unity. Experiments of the author in total absorption (to be described in a subsequent paper) show them to be of the same order of intensity. In fact, the lines in total absorption show that the ratios do not follow a rational scheme. After some lines have shown a steady decrease in intensity, there is a pair of lines of almost same intensity, and the experimental errors are such that we cannot definitely say which is the stronger and which the weaker of the two.

4. An interesting point from the calculations appears to be the extreme weakness of the line (5). The ratio of f-values of fourth and fifth lines is more than 500. There appears to be no chance for its verification. The experimental value from absorption is even less than two. The theory will have to be modified in the fundamentals, and probably exchange effects will lead to the right order results. So far as the theory outlined above goes, the consistency of the work will be apparent from the following argument.

Hargreaves (*loc. cit.*) has shown that the *f*-value of a line ending at a higher level with large n can be approximately determined if we know the rate of variation of the *f*-value at the series limit.

$$f_{n'\to n}=\frac{C}{n^3}\left(\epsilon_0-\frac{1}{n^2}\right) \qquad \ldots (12)$$

where n' is the ground state, and ϵ_0 is the term-value in hcR units. C is given by the relation

$$C=\frac{2}{\epsilon_0}\left(\frac{df}{d\epsilon}\right)_{\text{series limit.}} \qquad \ldots (13)$$

Miss Phillips has calculated $\left(\frac{df}{d\epsilon}\right)$ at series limit for potassium atom to be .0024. Substituting this in above, we get

$$f_{n'\to 8}=\frac{2\times .0024}{.319}\ \frac{(.319-1/64)}{8^3}=8.9\times 10^{-6}.$$

which compares favourably with the theoretical value 6.6×10^{-6}.

5. The calculated *f*-values suggest a very large continuous absorption from the requirements of the *f*-sum rule. The rule states for Potassium atom in the normal state :—

$$\sum_{n=4}^{\infty} f_{4,\,0\to n,\,1}+(f)_{\text{cont}}-f_{4,\,0\to 2,\,1}-f_{4,\,0\to 3,\,1}=1 \qquad \ldots (14)$$

lines 4, 0 to 4, 1 to 4, 0 to 8, 1 have been evaluated. The sum for the remaining lines

$\sum_{n=8}^{\infty} f_{4,\,0\to n,\,1}$ can be found from the $\frac{1}{n^3}$ law and its value is 2.6×10^{-3}.

Substituting in above we get, $(f)_{\text{cont}}=\cdot 05$ (empirical field) and it is still larger for Hartree field. But the value obtained from integration of the curve obtained by Miss Phillips is only .0002. This might mean that extrapolation of this curve showing monotonic decrease is not warranted. The experimental observations of Ditchburn recording this increase in continuous absorption support this view. But regarding the explanation of the increase being in a region far beyond the series limit, further calculation including exchange effects are needed.

CONCLUSION

The *f*-values of few members of the principal series lines of potassium have been determined and *f*-value for continuous absorption inferred. A glance at these values shows the arbitrary relation between the *f*-ratios and the line numbers. The calculations are, however, for a single atom. In order to examine the theory critically, the experiments must be carried on at very low vapour pressures and with no disturbing foreign gases. But it is not easy to conduct such experiments, since quartz windows on the absorption tube are

attacked by potassium vapour and so the ends of the tubes have to be kept cold. This necessitates the use of some foreign gas to guard against rapid distillation of the metal to the cooler portions. Further at low vapour pressures and low foreign gas pressures the lines are very fine and their photometric measurements are very difficult. For quantitative measurements we, therefore, need broad lines. How far the broadening agents effect the *f*-values, has yet to be investigated in detail.

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